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Symmetry reduction of δ-plutonium: an electronic-structure effect

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ABSTRACT

Using first-principles density-functional theory calculations, we show that the anomalously large anisotropy of δ-plutonium is a consequence of greatly varying bond-strengths between the 12 nearest neighbors. Employing the calculated bond strengths, we expand the tenants of classical crystallography by incorporating anisotropy of chemical bonds, which yields a structure with the monoclinic space group *Cm* for δ-plutonium rather than face-centered cubic $Fm\bar{3}m$. The reduced space group for δ-plutonium enlightens why the ground state of the metal is monoclinic, why distortions of the metal are viable, and has considerable implications for the behavior of the material as it ages. These results illustrate how an expansion of classical crystallography that accounts for anisotropic electronic structure can explain complicated materials in a novel way.

INTRODUCTION

Classical crystallography does not incorporate anisotropy of atomic bonds within its framework [1]. Rather, it assumes a spherical atom at each lattice site. While this assumption is justifiable for some elements, it becomes less reliable for those with complicated electronic structures. Nowhere is this more the case than with plutonium, which is the most enigmatic metal in the Period Table [2-8]. Recently, the phonon dispersion curves for single-grain δ-plutonium were recorded using inelastic X-ray scattering [9], confirming other measurements [10,11] that it is the most anisotropic face-centered cubic (fcc) metal known. The shear moduli C_{44} and C′ differ by a factor of ~7, which is in strong contrast to aluminum exhibiting a factor of 1.2 [12]. In addition, δ-Pu has a negative coefficient of thermal expansion and has the most crystallographically expanded lattice of all six Pu allotropes (fcc is usually the most densely packed crystal structure). This is evidence that a simple hard-sphere assumption is inappropriate for Pu and that the bonding strengths between the 12 nearest neighbors of the fcc δ-Pu lattice are not equal. In turn, this means that the total symmetry of the metal may not be fcc, but rather a lower symmetry class.

Here, we present a novel use of first-principles calculations, which yields the bond strengths of the 12 nearest neighbors within the δ-Pu crystal. Using these calculated bond strengths, we systematically progress through crystallographic arguments showing that δ-Pu belongs to the monoclinic space group *Cm* rather than the cubic $Fm\bar{3}m$ space group. Our results provide new insight into why plutonium is the only metal with a monoclinic ground state and why tetragonal, orthorhombic, or monoclinic distortions of δ-Pu are likely. These distortions have considerable ramifications for the behavior of the metal as it ages, accumulating damage via self-

irradiation. Finally, we anticipate the use of these calculations and crystallographic arguments in tandem [13] will expand crystallographic determination of complicated materials to incorporate electronic structure, consequently providing a unique way to explain complex properties.

CALCULATIONAL DETAILS

For Pu bond strengths, full-potential linear-muffin-tin orbital FPLMTO calculations [14] were employed, since these have been used extensively and successfully for transition [15] and actinide [16] metals. The "full potential" refers to the use of non-spherical contributions to the electron charge density and potential. This is accomplished by expanding these in cubic harmonics inside non-overlapping muffin-tin spheres and in a Fourier series in the interstitial region. We use two energy tails associated with each basis orbital and for the semi-core $6s$, $6p$, and valence $7s$, $7p$, $6d$, and $5f$ states, these pairs are different. Spherical harmonic expansions are carried out through $l_{max} = 6$ for the bases, potential, and charge density. For the electron exchange and correlation energy functional, the generalized gradient approximation (GGA) is adopted [17,18]. The nearest-neighbor bond strengths are obtained from total energy calculations of a 27-atom super cell that uniquely defines all 12 nearest neighbors (NN). By introducing a small (2%) displacements, along each of the 12 NN bonds, the force associated with the respective bond is obtained from the corresponding energy shift scaled by the magnitude of the displacement. This is the 'bond strength.' The super-cell is allowed to spin polarize ferromagnetically, whereas spin-orbit interaction is omitted to simplify the calculations. Integration over the irreducible wedge of the Brillouin zone (IBZ, $1/4^{th}$ of the full zone) is performed using the special k-point method [19] and we used 20 k points in the IBZ for the fcc super-cell.

RESULTS AND DISCUSSION

Let us begin with a two-dimensional array of blocks, as shown in Figure 1 (a and b). First, a square array of points is created, which is the *lattice*. Blocks are then incorporated around each lattice point, which is the *motif*. The resulting structure is shown Figure 1 (a). The combination of a lattice and motif in two dimensions results in a *plane group*, the two-dimensional analog to a *space group* for three-dimensions. This two-dimensional structure in Figure 1 (a) has a plane group symmetry of 4*mm* because there is an axis of 4-fold rotation about each lattice point and there are four mirror planes marked m_1, m_2, m_3, and m_4. When the upper-left and lower-right corners of each block are filled, the motif is altered. The plane group symmetry of this structure is accordingly reduced to 2*mm* because of the loss of 4-fold symmetry and the elimination of the m_1 and m_2 mirror plane planes. The important point here is that the structure in 1(b) still has a square lattice, even though the axis of 4-fold symmetry is lost and the total symmetry of the structure is reduced.

An example of this idea in three dimensions and in a real crystal is the body-centered cubic (bcc) structure of α-iron. When paramagnetic, the structure has a bcc space group of Im$\bar{3}$m. However, when the crystal structure becomes ferromagnetic with aligned moments in the [001] direction the symmetry is reduced to *I4/mm'm'*, as shown in Figure 2 [20]. From a geometry
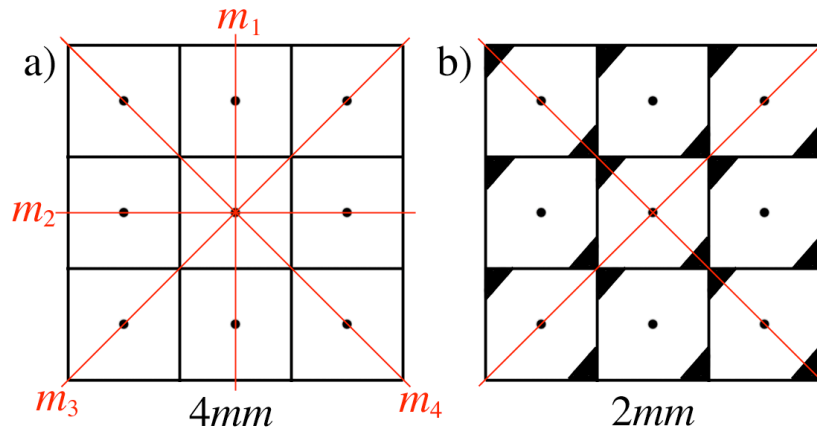
Figure 1. Two periodic arrays illustrating repetition of a lattice (points) and a motif (blocks). (a) a pattern showing a plane group symmetry of 4*mm* and (b) a pattern showing a plane group symmetry of 2*mm*, reduced only by a change in the motif, not the lattice.

standpoint $a = b = c$, but the fact that the spins are aligned along the z-axis lowers the symmetry of the crystal structure. Thus, there does not need to be atomic displacements, and correspondingly a change in lattice, to reduce the symmetry of the structure. Accurate orbital magnetic moments of bcc iron cannot be obtained from calculations [21] unless considering a lowering of the symmetry, from 48 (cubic) to 16 (tetragonal) operations, due to the preferred orientation of the magnetic spin moments along the [001] easy axis.
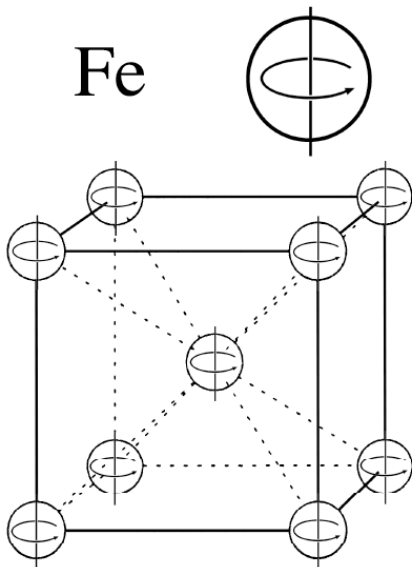

Figure 2. The structure of α-iron. The crystal has a body-centered cubic space group of $Im\bar{3}m$ when paramagnetic, but is reduced to $I4/mm'm'$ when the crystal becomes ferromagnetic with aligned moments in the [001] direction.

In the case of the two-dimensional array of blocks in Figure 1 (plane group) or in the three-dimensional bcc structure of α-iron (space group), the same point comes out: the lattice itself may remain high symmetry, but the crystal structure as a whole may be reduced in symmetry due to a change in motif. This is because the symmetry of any plane or space group is composed of the intersection of the symmetries of a lattice and a motif. In ferromagnetic α-iron, the magnetic moment produced by the outermost valence electrons not only degrades the symmetry from bcc to tetragonal, but also alters the macroscopic properties that we observe, such as elastic constants, shear modulus, and phase transformations. While a magnetic moment can reduce symmetry as described above, other aspects of the outermost bonding electrons can also affect the symmetry.

Armed with this knowledge, let us return to the case of δ-Pu. We begin with the assumption that the lattice is fcc with $a = b = c$. A motif is then created, which is the bond strengths for the 12 nearest neighbors. The question is, if an fcc lattice is joined with a motif of anisotropic bonds, what is the resultant space group? In order to resolve this issue the detailed electronic structure of Pu must be determined, and in particular the variation of the nearest-neighbor bond strengths. This was performed by calculating the energy response (ΔE) of a 2% displacement of an atom along each of the 12 nearest-neighbor directions and scaling this with the displacement magnitude (u = 0.049Å), as described in the methods section. Density-functional theory has proven to be accurate for most metals in the Periodic Table, including Pu [22], however, its use for calculating bond strength is entirely unique.

Nearest Neighbor (x,y,z)	Miller Indices (h,k,l)	ΔE (mRy/atom)	ΔE/u
0.5 0.5 0	110	0.230	4.69
-0.5 -0.5 0	-1-10	0.220	4.49
0.5 -0.5 0	1-10	0.180	3.67
-0.5 0.5 0	-110	0.170	3.47
0.5 0 0.5	101	0.200	4.08
-0.5 0 -0.5	-10-1	0.160	3.27
-0.5 0 0.5	-101	0.230	4.69
0.5 0 -0.5	10-1	0.190	3.88
0 -0.5 0.5	0-11	0.190	3.88
0 0.5 -0.5	01-1	0.160	3.27
0 0.5 0.5	011	0.260	5.31
0 -0.5 -0.5	0-1-1	0.180	3.67

Table 1. The nearest neighbor direction in x, y, z coordinates, Miller indices (h,k,l), change in energy (ΔE) due to a 2% shift of a 0,0,0 atom, and the change in energy normalized by the displacement length (ΔE/u).

The results of the calculations are shown in Table 1 and Figure 3. The nearest neighbor direction (x,y,z), Miller indices (h,k,l), change in energy (ΔE) due to a 2% shift of the 0,0,0 atom, and the change in energy normalized by the displacement length (ΔE/u) are shown in Table 1.

Notice how ΔE/u varies from ~3.3 to ~5.3, showing the large degree of variation in bond strength between the 12 nearest neighbors. As shown in Figure 3, the twelve nearest neighbors can be separated into six pairs of two where the bond strengths are close in value: blue (3.3), black (3.5-3.7), red (3.7-3.9), pink (3.9-4.1), green (4.5-4.7), and brown (4.7-5.3). In the (001) plane, the [110] bond is roughly equal to the [$\bar{1}\bar{1}$0] bond (green), and the [$\bar{1}$10] bond is roughly equal to the [1$\bar{1}$0] bond (black). In the {011} planes, we see that [01$\bar{1}$]~[$\bar{1}$01] (blue), [0$\bar{1}$1]~[$\bar{1}$0$\bar{1}$] (red), [0$\bar{1}\bar{1}$]~[101] (pink), and [011]~[$\bar{1}$0$\bar{1}$] (brown). It is important to note that not only the bond strength, but also the repeatability of groupings dictate the choice of sets. In other words, there is a clear separation between the brown and pink sets and the clear separation between the red and blue sets. It is interesting that the bonds in the (001) plane are almost equal directly across the central atom, whereas the bonds in the {011} planes are not and have a more complicated arrangement.
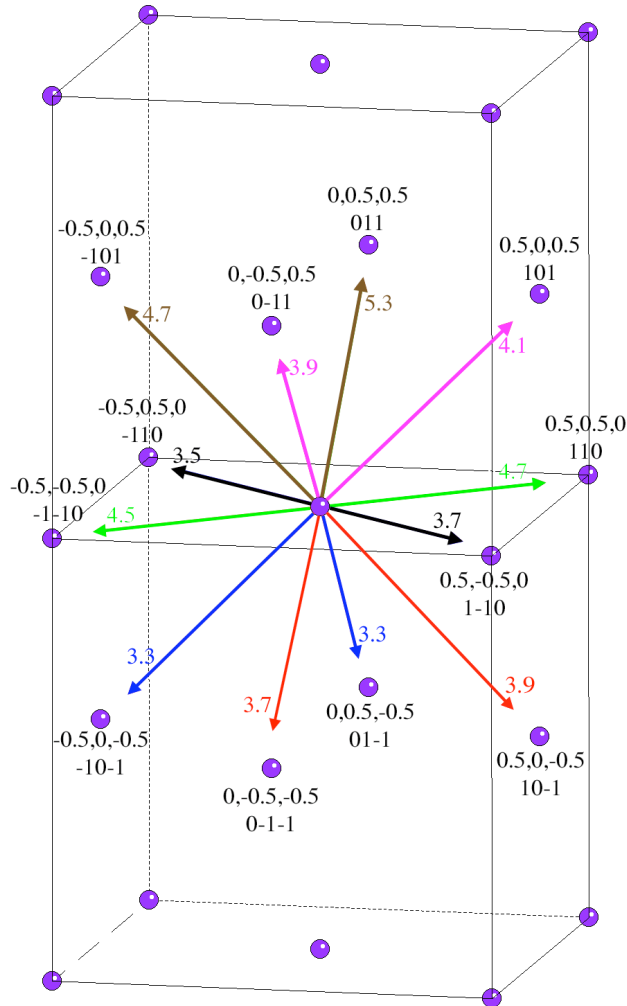

Figure 3. Two stacked fcc unit cells with the central atom showing the 12 nearest neighbors. In the case of plutonium, the 12 bonds with the nearest neighbors widely vary with strength and can be separated into six pairs. When the fcc lattice is combined with the motif of these bond strengths the resultant structure is monoclinic *Cm*.

When an fcc lattice is joined with the calculated bond strengths as a motif, the resultant structure is *c*-centered monoclinic with the space group *Cm*. This low symmetry space group is due to the fact that besides translational symmetry there is no rotational symmetry and only one mirror plane along the (110) plane. The new Bravais lattice for the structure is shown in Figure 7, where (a) is the three-dimensional rendering of the *c*-centered unit cell and (b) is a two-dimensional rendering viewed along the [001] direction. In (b) the fcc lattice is shown by the purple box. The *c*-centered unit cell is shown by the heavy red box with the green line marking the [110] mirror plane.
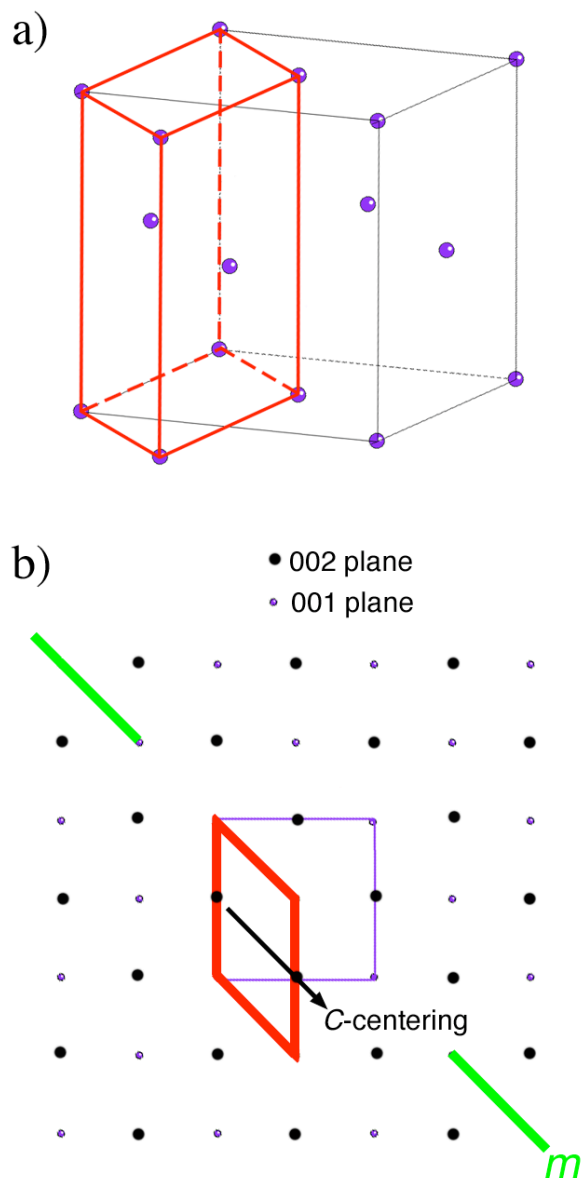
a)

b)

Figure 7. (a) Three-dimensional and (b) two-dimensional representations of the c-centered monoclinic Bravais Lattice needed to fully describe δ-Pu.

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This space group has several ramifications. First, it now seems no coincidence that the ground state α-phase of Pu is monoclinic $P2_1/m$ and that here we show δ-Pu exhibits a monoclinic space group of Cm when the bonding strengths are accounted for as the motif. Also, β-Pu is $C2/m$, where the only difference between the two space groups $C2/m$ and Cm is an axis of two-fold rotation perpendicular to the mirror plane. (Of course, in the real structures there is also a slight change of atomic positions). The reduced space group of Cm for δ-Pu yields a viable path for the $\delta \leftrightarrow \alpha'$ phase transformation of Pu and Pu alloys. It has been shown that at low pressures (~ 0.4 GPa) δ transforms first to β' then to α' in Pu-Ce [23] and Pu-Al [24] alloys. Given how close the space groups are between the reduced space group of Cm for δ-Pu and $C2/m$ β-Pu, this intermediate transformation to β makes sense.

A second important consequence of these calculations is that the structure is not centrosymmetric (defined as: $x = -x$; $y = -y$; $z = -z$). Classical crystallography assumes spherical atoms occupy each lattice site and that fcc crystals are centrosymmetric However, the above arguments show that this is a flawed idea for δ-Pu. The electronic structure (dominated by $5f$ states) produces bonding in δ-Pu with largely varying strength between the 12 nearest neighbors, thus making the crystal highly anisotropic and one that is the least applicable candidates for centrosymmetry compared to other fcc metals.

If one is to imagine a spectrum of isotropy, aluminum would reside on one side and plutonium on the other. With this in mind, we performed the same calculations on aluminum, which is well known to be the most isotropic fcc metal [25,26]. The results, which are in the same units as the Pu results, lie within 7.55-7.57 for the nearest-neighbor bond strengths. The slight variation in the resulting numbers is numerical noise. In other words, the method used above shows aluminum to have bond strengths for the 12 nearest neighbors which are identical, further supporting that Al is a highly isotropic metal.

The reduction of symmetry of δ-Pu illustrated above clarifies recent experimental results, such as those from Lawson *et al.* [27,28] that suggest a tetragonal distortion occurs in Ga-stabilized δ-Pu. In the work by Lawson *et al.* [27,28], neutron diffraction revealed that the widths of the peaks were temperature dependent for $Pu_{0.98}Ga_{0.02}$. As the sample was cooled, peak broadening occurred, increasing with subsequent cooling cycles. This affect disappeared when heated to 650K. The diffraction peaks were anisotropic, which were modeled by assuming a small tetragonal distortion to the crystal. Because the changes of the diffraction peaks were observed at low temperature, it is possible that they are due to the anisotropic response of the δ-Pu matrix to the ingrowth of monoclinic α'-Pu particles that form during an isothermal martensitic phase transformation at low temperatures [29]. If one introduces precipitates or defects such as vacancies, interstitials, dislocations, and/or He bubbles [30] into an anisotropic medium, the variation in bond strength will cause the lattice to extend more in the soft directions and less in the rigid directions. Thus, tetragonal, orthorhombic, or monoclinic distortions in aged Ga-stabilized δ-Pu are logical, because precipitation of second-phase particles or the accumulation of damage will strain the lattice and contract/expand it disproportionately in different directions. Also to note is the small value of C' for δ-Pu [9,31,32], which implies a soft response of the system to a volume-conserving tetragonal distortion.

Another interesting observation was that of Cox *et al.* [33], where extended X-ray absorption fine-structure spectroscopy was applied to Ga-stabilized δ-Pu. In these experiments it was observed that the local structure of plutonium about the Ga atoms was well defined and quite similar to a typical fcc metal. However, the local structure of plutonium around Pu atoms was

disordered, especially in the individual shells at radii greater than 3.5Å. This means that there is a complexity in the distribution of the neighboring atoms in the successive shells around each Pu atom, and the authors ascribe this to local distortion of the Pu-Pu bonds in the vicinity of Ga impurities. This again shows that when under stress, δ-Pu distorts in such a way as to lose its fcc crystal structure, likely due to the 12 nearest neighbor bonds having markedly different strengths.

The two examples above were for δ-Pu in a perturbed system, and its anisotropic response. However, the question arises what does the symmetry of δ-Pu appear as experimentally while under normal conditions? This can be interrogated using high-resolution synchrotron-radiation-based x-ray diffraction. While x-ray diffraction does not measure bond energies, it does measure electron charge density. The x-ray scattered intensity for a given reflection is determined by the Fourier transform of the charge density [34]. In the case where there is a spherical (isotropic) and non-spherical (anisotropic) part, each can be separated and calculated. The spherical part will be much larger than the non-spherical part, and a rough calculation of the difference in intensity can be obtained by $(1/Z)^2$. In the case of Pu, any additional reflection due to anisotropic distribution of the valence electrons would be approximately 1×10^{-4} weaker than the primary reflections. In reality, additional reflections are probably more on the order of 1×10^{-5} to 1×10^{-6} weaker, and the above simple equation is more accurate for light elements. We predict that either 1) additional reflections or 2) highly asymmetric primary reflections should occur due to a reduction of symmetry, and that these effects should be detectable with present synchrotron sources and detectors [35].

In conclusion, we have shown that when a fcc lattice is joined with the calculated anisotropic bonding of the 12 nearest neighbors as the motif (lattice + motif = space group) the resultant space group of δ-Pu is *Cm* rather than *Fm3̄m*. This approach uses first-principles in a novel way, and goes beyond the tenets of classical crystallography by incorporating anisotropic chemical bonds. Our results enlighten why α-Pu is the only metal with a monoclinic ground state, reveal that δ-Pu does not have a center of symmetry, and lend a fundamental explanation for the tetragonal distortion purported to occur in Ga-stabilized δ-Pu as defects are introduced or as lattice damage is accumulated. Finally, these results systematically illustrate that an expansion of classical crystallography that accounts for anisotropic electronic structure can be used to explain complicated materials in a way previously not utilized.

ACKNOWLEDGEMENTS

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